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Ikuzo Tanaka, declare as follows:

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2. To the best of my ability, I translated

Japanese Patent Application No. 9-358552

from Japanese into English and the attached document is a true and accurate English translation thereof.

3. I further declare that all statements made herein are true, and that all statements made on information and belief are believed to be true; and further that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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FERRITE MAGNET AND METHOD FOR PRODUCING SAME

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**Attached Papers**

Specification one

Drawings one

ABSTRACT one

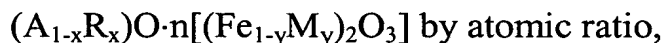
## SPECIFICATION

### Title of the Invention

FERRITE MAGNET AND METHOD FOR PRODUCING SAME

### 5 Claims

1. A ferrite magnet having a basic composition represented by the following general formula:



wherein A is at least one of Sr and Ba, R is at least one element selected  
10 from the group consisting of La, Nd and Pr, La being an indispensable  
element, M is at least one element selected from the group consisting of  
Mn, Co and Ni, and x, y and n are numbers meeting the following  
conditions:

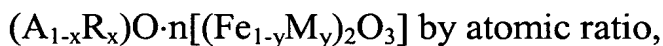
$$0.05 \leq x \leq 0.5,$$

15  $[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$

$$5.4 \leq n \leq 6.0.$$

2. The ferrite magnet according to claim 1, further comprising  
0.20-0.50 weight % of SiO<sub>2</sub> and 0.35-0.55 weight % of CaO per said basic  
composition.

20 3. A ferrite magnet having a basic composition represented by the  
following general formula:



wherein A is at least one of Sr and Ba, R is at least one element selected  
from the group consisting of La, Nd and Pr, La being an indispensable  
25 element, M is at least two elements selected from the group consisting of

Mn, Co, Ni and Zn, Co being an indispensable element, and x, y and n are numbers meeting the following conditions:

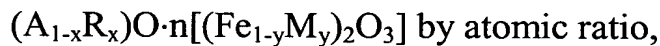
$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

5  $5.4 \leq n \leq 6.0.$

4. The ferrite magnet according to claim 2, further comprising 0.20-0.50 weight % of SiO<sub>2</sub> and 0.35-0.55 weight % of CaO per said basic composition.

5. A method for producing a ferrite magnet having a basic  
10 composition represented by the following general formula:



wherein A is at least one of Sr and Ba, R is at least one element selected from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least one element selected from the group consisting of  
15 Mn, Co and Ni, and x, y and n are numbers meeting the following conditions:

$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

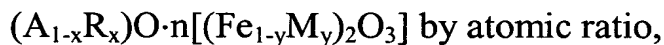
$$5.4 \leq n \leq 6.0,$$

20 said method comprising the steps of subjecting a raw material powder having said basic composition to pulverizing to a fine powder having an average diameter ranging 0.4-0.7  $\mu$ m, drying or concentrating, milling, molding in a magnetic field and sintering.

6. The method producing a ferrite magnet according to claim 5,  
25 wherein 0.2-2.0 weight % of a dispersant per a solid component is added at

the time of pulverizing or milling.

7. A method for producing a ferrite magnet having a basic composition represented by the following general formula:



5 wherein A is at least one of Sr and Ba, R is at least one element selected from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least one element selected from the group consisting of Mn, Co, Ni and Zn, Co being an indispensable element, and x, y and n are numbers meeting the following conditions:

$$10 \quad 0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5.4 \leq n \leq 6.0,$$

said method comprising the steps of subjecting a raw material powder having said basic composition to pulverizing to a fine powder having an  
15 average diameter ranging 0.4-0.7  $\mu\text{m}$ , drying or concentrating, milling, molding in a magnetic field and sintering.

8. The method producing a ferrite magnet according to claim 7, wherein 0.2-2.0 weight % of a dispersant per a solid component is added at the time of pulverizing or milling.



## DETAILED DESCRIPTION OF THE INVENTION

[0001]

### Field of the Invention

The present invention relates to a high-performance ferrite magnet  
5 useful for wide ranges of magnet applications and having a higher  
saturation magnetization ( $\sigma_s$ ) and higher coercivity ( $iH_c$ ) than those of the  
conventional ferrite magnets, and a method for producing such a  
high-performance ferrite magnet.

[0002]

### 10 Prior Art

Ferrite magnets are widely used in various applications including  
rotors of motors, electric generators, etc. Recently, ferrite magnets having  
higher magnetic properties are required particularly for the purposes of  
miniaturization and reduction in weight in the field of rotors for  
15 automobiles and increase in performance in the field of rotors for electric  
apparatuses.

High-performance sintered magnets such as Sr ferrite or Ba ferrite  
are conventionally produced through the following processes. First, iron  
oxide is mixed with a carbonate, etc. of Sr or Ba and then calcined to cause  
20 a ferritization reaction (ferrite-forming reaction). The resultant calcined  
clinker is coarsely pulverized, mixed with  $SiO_2$ ,  $SrCO_3$  and  $CaCO_3$  for  
controlling sintering behavior and  $Al_2O_3$  or  $Cr_2O_3$ , etc. for controlling  $iH_c$ ,  
and then finely pulverized to an average diameter of 0.7-1.0  $\mu m$ . A slurry  
containing the finely pulverized ferrite-forming material is wet-molded  
25 while being oriented in a magnetic field to obtain a mold. The resultant

mold is sintered and then machined to a desired shape.

[0003]

### **Problems to be Solved by the Invention**

To increase the properties of the ferrite magnets produced according to the method mentioned above as a prerequisite, there are the following five methods available.

The first method is a fine pulverization method. When the size of crystal grains in the sintered body is close to about  $0.9\ \mu\text{m}$ , a critical single magnetic domain diameter of a magnetoplumbite (M)-type Sr ferrite magnet, its  $iH_c$  is maximum. Accordingly, fine pulverization may be carried out to an average diameter of  $0.7\ \mu\text{m}$  or less, for instance, taking into consideration the crystal grain growth at the time of sintering. This method is, however, disadvantageous in that finer pulverization leads to poorer water removal at the time of wet molding, resulting in poorer production efficiency.

The second method is to make the sizes of the crystal grains in the sintered body as uniform as possible. Ideally, the sizes of the crystal grains are made as uniformly as possible equal to the above critical single magnetic domain diameter (about  $0.9\ \mu\text{m}$ ), because crystal grains larger than or smaller than this size have low  $iH_c$ . Specific means for achieving high performance in this method is to improve a particle size distribution of fine powder. In commercial production as a prerequisite, however, other pulverization apparatuses than ball mills, attritors, etc. cannot be used, naturally posing limitations in the level of improvement. Also, an attempt was recently published to produce fine ferrite powder having a uniform

particle size by a chemical precipitation method. Such method is, however, not suitable for industrial mass production.

The third method is to improve crystal orientation affecting magnetic anisotropy. Specific means in this method is to improve the  
5 dispersion of ferrite particles in a slurry of fine powder by adding a surfactant, or to increase the intensity of a magnetic field at the time of orientation, etc.

The fourth method is to improve the density of a sintered body. A Sr ferrite sintered body has a theoretical density of 5.15 g/cc. Sr ferrite  
10 magnets commercially available at present have densities ranging from 4.9 g/cc to 5.0 g/cc, corresponding to 95-97% of the theoretical density. Although improvement in Br is expected by increasing the density of a ferrite magnet, a higher density than the above level needs such density-increasing means as HIP, etc. However, the use of such  
15 density-increasing means leads to increase in the production cost of ferrite magnets, depriving the ferrite magnets of advantages as inexpensive magnets.

The fifth method is to improve a saturation magnetization  $\sigma_s$  or a crystal magnetic anisotropy constant of a ferrite compound per se, which is  
20 a main component of the ferrite magnet. It is likely that the improvement in the saturation magnetization  $\sigma_s$  directly leads to improvement in the residual magnetic flux density Br of the ferrite magnet. It is also likely that the improvement in the crystal magnetic anisotropy constant leads to improvement in the coercivity Hc of the ferrite magnet. The conventional  
25 ferrite compound has an M-type (magnetoplumbite-type) crystal structure.

Although research is being carried out on W-type ferrite having a higher saturation magnetization than that of the M-type ferrite, the W-type ferrite has not been subjected to mass production because of difficulty in the control of a sintering atmosphere.

5           Widely used at present among the above methods for improving the properties of ferrite magnets are the first to fourth methods, though it is difficult to drastically improve the properties of ferrite having a main phase expressed by  $\text{SrO} \cdot n\text{Fe}_2\text{O}_3$  by the first to fourth methods for the reasons described below. The first reason is that the above first to fourth methods  
10 include conditions lowering productivity or steps difficult to carry out from the aspect of mass production. The second reason is that further improvement in magnetic properties, particularly Br, is extremely difficult because they are close to the theoretically highest level.

Accordingly, an object of the present invention is to provide a new  
15 ferrite magnet excellent remarkably in magnetic properties and a method for producing thereof based on the above fifth method.

[0004]

#### **Means to Solve the Problems**

To achieve the above object, in the present invention, there has been  
20 found a method to replace part of A and Fe elements in the above ferrite composition with other elements by adding other types of metal compounds to a ferrite composition expressed by  $\text{AO} \cdot n\text{Fe}_2\text{O}_3$ , wherein A is at least one of Sr and Ba.

The magnetism of the magnetoplumbite-type ferrite magnet is  
25 derived from a magnetic moment of Fe ions, with a magnetic structure of a

ferri-magnet in which magnetic moment is arranged partially in antiparallel by Fe ion sites. There are two methods to improve the saturation magnetization in this magnetic structure. The first method is to replace the Fe ions at sites corresponding to the antiparallel-oriented magnetic  
5 moment with another element, which has a smaller magnetic moment than Fe ions or is non-magnetic. The second method is to replace the Fe ions at sites corresponding to the parallel-oriented magnetic moment with another element having a larger magnetic moment than Fe ions.

Also, increase in a crystal magnetic anisotropy constant in the  
10 above magnetic structure can be achieved by replacing Fe ions with another element having a stronger interaction with the crystal lattice. Specifically, Fe ions are replaced with an element in which a magnetic moment derived from an orbital angular momentum remains or is large.

With the above findings in mind, an enormous research has been  
15 conducted in detail for the purpose of replacing Fe ions with various elements by adding various metal oxides. As a result, it has been found that Mn, Co, Ni and Zn are elements remarkably improving magnetic properties. However, the mere addition of the above elements would not provide ferrite magnets with fully improved magnetic properties, because  
20 the replacement of Fe ions with other elements would destroy the balance of ion valance, resulting in the generation of undesirable phases. To avoid this phenomenon, ion site of Sr or Ba should be replaced with other elements for the purpose of charge compensation. Thus, it has been revealed that, for this purpose, the addition of Nd, Pr, etc., particularly, La  
25 is effective. The present invention has been completed based upon this

finding.

[0005]

Thus, the ferrite magnet the present invention has a basic composition represented by the following general formula:

5  $(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,  
wherein A is at least one of Sr and Ba, R is at least one element selected from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least one element selected from the group consisting of Mn, Co and Ni, and x, y and n are numbers meeting the following  
10 conditions:

$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5.4 \leq n \leq 6.0.$$

In the ferrite magnets of the present invention, the percentage of La  
15 in R is preferably 50 atomic % or more, more preferably 70 atomic % or more, particularly preferably 99 atomic % or more, and to improve saturation magnetization thereof, the R element may be ideally composed of La only. The M element may be composed of any one of Mn, Co and Ni. However, to obtain higher iHc, Co is most preferable.

20 Also, the ferrite magnet the present invention has a basic composition represented by the following general formula:

$$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3] \text{ by atomic ratio,}$$

wherein A is at least one of Sr and Ba, R is at least one element selected from the group consisting of La, Nd and Pr, La being an indispensable  
25 element, M is at least two elements selected from the group consisting of

Mn, Co, Ni and Zn, Co being an indispensable element, and x, y and n are numbers meeting the following conditions:

$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

5  $5.4 \leq n \leq 6.0.$

In this case, the feature of the present invention includes a double replacement such that the M element may be composed of at least 2 elements selected from the group consisting of Mn, Co, Ni and Zn, and Co is always contained, however to improve saturation magnetization thereof, the Co content in the M element is preferable 50 atomic % or more, more preferably 70 atomic % or more.

To impart good magnetic properties to the ferrite magnet of the present invention, the value of n (molar ratio) should be between 5.4 and 6.0. When the value of n exceeds 6.0, undesirable phases such as  $\alpha\text{-Fe}_2\text{O}_3$  other than the magnetoplumbite phase are generated, resulting in drastic decrease in magnetic properties. On the other hand, when the value of n is less than 5.4, sufficiently good Br of the ferrite magnet cannot be obtained.

Also, the value of x is between 0.05 and 0.5. When the value of x is less than 0.05, sufficient effects related to the method of the present invention cannot be obtained. On the other hand, when the value of x exceeds 0.5, the magnetic properties of the ferrite magnet rather decrease.

With respect to the relations between the value of x and that of y, to attain the object of the charge compensation, it is necessary to satisfy the relation of  $y = x/(2.0n)$ .

When the value of  $y$  is between  $x/(1.6n)$  and  $x/(2.4n)$ , the effects of the present invention are not substantially impaired. When value of  $y$  deviates from  $x/(2.0n)$ , there is likelihood that  $\text{Fe}^{2+}$  is contained, though there are no problems.

5 [0006]

In the standard process for producing ferrite magnets essentially comprising the steps of

mixing of starting material powders → calcination → fine

pulverization of calcined powder → molding → sintering,

10 the above basic composition of the ferrite magnet may be substantially achieved at the calcination step.

That is, the R element and the M element are to undergo two time heating at a high temperature at the time of calcination and sintering by adding at the time of mixing in the above steps, whereby the solid diffusion  
15 proceeds to provide a uniform composition. However, it is not substantially destroy the effects of the present invention to obtain substantially the same ferrite magnet composition as the chemical formula recited in claim 1 of the present application by adding oxides of the R element and oxides of the M element at the time of pulverizing in the above  
20 standard process for producing.

To obtain the high-performance ferrite sintered body, it is preferable to add  $\text{SiO}_2$  and  $\text{CaO}$  ( $\text{CaCO}_3$ ) as elements for controlling a sintering phenomenon at the pulverization step.

$\text{SiO}_2$  is an additive for suppressing crystal grain growth at the  
25 sintering step, and the amount of  $\text{SiO}_2$  added is preferably 0.20-0.5



weight %, assuming that the basic composition of the ferrite magnet is 100 weight %. When the amount of  $\text{SiO}_2$  added is less than 0.20 weight %, excessive crystal grain growth takes place at the sintering step, resulting in decrease in coercivity. On the other hand, when the amount of  $\text{SiO}_2$  added exceeds 0.50 weight %, crystal grain growth is excessively suppressed, resulting in insufficient improvement in orientation that occurs simultaneously with the crystal grain growth, which leads to decrease in the residual magnetic flux density (Br).

On the other hand, CaO is an element for accelerating the crystal grain growth, and the amount of CaO added is preferably 0.35-0.55 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %. When the amount of CaO added exceeds 0.55 weight %, excessive crystal grain growth takes place at the sintering step, resulting in decrease in coercivity (iHc). On the other hand, when the amount of CaO added is less than 0.35 weight %, crystal grain growth is excessively suppressed, resulting in insufficient improvement in orientation that occurs simultaneously with the crystal grain growth, which leads to decrease in Br. [0007]

To obtain the further high-performance ferrite sintered body, it is preferable to produce it by the following method in place of the above standard process. Namely, it is preferable to choose a technical means such that the above basic composition of the ferrite magnet is subjected to wet pulverizing until the average diameter of the powder mixture becomes 0.4-0.7  $\mu\text{m}$ , and a slurry of finely pulverized powder is concentrated or dried, crumbled, milled, wet-molded and then sintered.

When pulverization is carried out to an average diameter of less than  $0.4\ \mu\text{m}$ , undesirable crystal grain growth takes place at the sintering step, resulting in decrease in coercivity and the deterioration of water removal characteristics at the wet-molding step. Also, when the average  
5 diameter of the powder exceeds  $0.7\ \mu\text{m}$ , there are a lot of coarse crystal grains in the structure of the ferrite sintered body.

The important requirements for obtaining the high-performance ferrite magnet are that the composition of the ferrite powder used should be properly controlled, and that the ferrite powder should not be agglomerated  
10 in a slurry. As a result of investigation to achieve a state in which each particle of the ferrite powder exists independently in the slurry, it has been found that the agglomeration of ferrite powder is destroyed due to application of a shearing force by drying or concentrating a ferrite powder slurry obtained by the wet-fine pulverization of ferrite powder, followed by  
15 adding a dispersant to the resultant high-concentration slurry and milling the slurry, resulting in improvement in orientation of ferrite magnet powder, which leads to improvement in magnetic properties. It has also been found that by adding a dispersant to the slurry at a mixing step, good dispersion can be achieved due to surface modification of ferrite magnet  
20 powder by the adsorption of the dispersant, resulting in further improvement in a magnetic force of the ferrite magnet.

Known as dispersants are surfactants, higher aliphatic acids, higher aliphatic acid soap, higher aliphatic acid esters, etc. It has been found that the dispersion of ferrite particles can be improved by using a  
25 polycarboxylic acid dispersant, one of anionic surfactants, effectively

preventing the agglomeration of ferrite particles. There are many types of polycarboxylic acid dispersants, and particularly effective for improvement in the dispersion of ferrite particles among them is an ammonium salt of polycarboxylic acid.

5 With respect to the amount of the dispersant per a solid component in the fine powder slurry, when the amount of the dispersant added exceeds 0.2 weight %, effects of adding the dispersant can be obtained. On the other hand, when it exceeds 2 weight %, the residual magnetic flux density of the ferrite magnet rather decreases.

10 [0008]

### Operative Embodiments for Practicing the Invention

The present invention will be described in detail below referring to EXAMPLES.

#### [EXAMPLE 1]

15  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ , oxides of R elements and oxides of M elements were formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{R}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 6.0$ ,  $x = 2ny$ , and  $x = 0.15$ ,

wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. La, Pr, Nd,

20 Sm, Eu and Gd were selected as the R element under the criterion that these elements had ion radii close to a radius of an Sr ion. Also, Ti, V, Mn, Co, Ni, Cu and Zn were selected as the M elements under the criterion that they had ion radii close to a radius of an Fe ion.

As COMPARATIVE EXAMPLE, a ferrite composition in which  $n =$   
25  $6.0$  and  $x = y = 0$  in the above basic composition was calcined in the same

manner.

Each calcined powder was coarsely pulverized in a dry state by a roller mill, and each of the resultant coarse powder was measured with respect to magnetic properties by a vibration-type magnetometer. The  
5 highest intensity of a magnetic field in which measurement was carried out was 12 kOe, and a saturation magnetization  $\sigma_s$  was determined by  $\sigma-1/H^2$  plot. The resultant phases of the coarse powder were identified by X-ray diffraction, with the results summarized in Table 1. It is appreciated from Table 1 that when Cu was not contained as the M element, only X-ray  
10 diffraction peaks for a magnetoplumbite phase (M phase) were observed in any powder. It is also appreciated from Table 1 that when La was selected as the replacement element in the R element, and Mn, Co, Ni or Zn was selected as the replacement element in the M element, respectively, the resultant calcined powder had higher  $\sigma_s$  or  $H_c$  than that in COMPARATIVE  
15 EXAMPLE, suggesting that such calcined powder had a potential that a high-performance, bulk ferrite magnet could be formed therefrom by sintering. Further, it is appreciated from Table 1 that when Mn + Co, Ni + Co and Zn + Co were selected as combined replacement elements with Co in the M element, the resultant calcined powder would have such a  
20 potential as to provide a higher performance, bulk ferrite magnet. On this occasion, the percentage of Co in the M elements is preferably 50 atomic % or more.

Also, when Pr, Nd, Sm, Eu or Gd were selected as the R element, and Zn were selected as the M element, respectively, the resultant calcined  
25 powder would expectedly have a potential to provide the same

high-performance, bulk ferrite magnet as in the case of selecting La as the R element with respect to Pr and Nd.

Incidentally, in the present invention, a combined replacement by the R elements such as La + Pr or La + Nd, etc. may further be used.

- 5 Among them, the percentage of La in the R elements is preferably 50 atomic % or more to have higher Br than that of the ferrite magnet in COMPARATIVE EXAMPLE.

[0009]

Table 1

No.	Composition (atomic %)		Magnetic Properties		Phase Produced
	R Element	M Element	$\sigma_s$ (emu/g)	H <sub>c</sub> (kOe)	
Ex. 1	La	100Ti	64.6	3.1	M Phase
Ex. 2		50Ti + 50Co	62.1	0.8	M Phase
Ex. 3		100V	59.0	6.4	M Phase
Ex. 4		50V + 50Co	59.1	6.4	M Phase
Ex. 5		100Mn	67.1	3.7	M Phase
Ex. 6		50Mn + 50Co	66.8	3.9	M Phase
Ex. 7		100Co	66.0	4.5	M Phase
Ex. 8		100Ni	66.1	2.9	M Phase
Ex. 9		50Ni + 50Co	65.9	3.5	M Phase
Ex. 10		100Cu	65.8	0.3	M Phase + Undesirable Phase
Ex. 11		50Cu + 50Co	65.1	1.2	M Phase + Undesirable Phase
Ex. 12		100Zn	68.9	3.1	M Phase
Ex. 13		50Zn + 50Co	67.8	3.6	M Phase
Com. Ex.	-	-	65.4	3.1	M Phase

[0010]

[EXAMPLE 2]

Sr, La and Co were selected as the A element, the R element and the M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{CoO}$  were  
 5 formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{Co}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 6.0$ ,  $x = 2ny$ , and  $x = 0-0.6$ ,

wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. Thereafter,  
 the coarse powder was produced by the method in the same manner as in  
 10 EXAMPLE 1, and the magnetic properties of the resultant coarse powder  
 were measured. The results are shown in Fig. 1.

It is appreciated from Fig. 1 that the simultaneous addition of  $\text{La}_2\text{O}_3$   
 and  $\text{CoO}$  remarkably improves coercivity ( $H_c$ ). Also, the saturation  
 magnetization ( $\sigma_s$ ) was substantially constant or no remarkable decrease in  
 15 its value. Further, when the value of  $x$  exceeded 0.05, its effects were  
 remarkable, and when the value of  $x$  exceeded 0.5, its effects decreased.  
 Thus, the value of  $x$  is preferably between 0.05 and 0.5, more preferably  
 between 0.07 and 0.4.

Also, when the R elements were  $\text{La} + \text{Pr}$  or  $\text{La} + \text{Nd}$  and the M  
 20 elements were  $\text{Co} + \text{Zn}$ ,  $\text{Co} + \text{Mn}$  or  $\text{Co} + \text{Ni}$ , the results indicated  
 substantially the same tendency as shown in Fig. 1.

Further, it has been confirmed that when the value of  $n$  was between  
 5.4 and 6.0, there was no significant difference, thereby obtaining the same  
 effects as mentioned above.

25 [0011]

## [EXAMPLE 3]

To investigate the permissible range of a ratio of the R element to the M element added in connection with charge compensation, Sr, La and Co were selected as the A element, the R element and the M element, respectively, and SrCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and CoO were formulated in such proportions as to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{Co}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 6.0$ ,  $y = 0.77-1.43 \times 10^{-2}$ , and  $x = 0.15$ ,

wet-mixed, and then calcined at 1200°C for 2 hours. Thereafter, the

coarse powder was produced by the method in the same manner as in EXAMPLE 1, and the magnetic properties of the resultant coarse powder were measured.

It has thus been found that there is no substantial deterioration in magnetic properties, as long as the ratio of  $x/ny$  is within the range of

1.6-2.4, not limited to the conditions under which the charge balance is fully kept, namely to a ratio of  $x$  to  $y$  satisfying the relation of  $y = x/2n$ .

On the other hand, when the ratio of  $x/ny$  exceeds 2.4 or is less than 1.6, remarkable decrease in magnetic properties is appreciated. Accordingly, the ratio of  $x/ny$  should be preferably between 1.6 and 2.4. This condition may be converted to the formula of  $y$  as a preferable range of the value of  $y$  as follows:

$$[x/(2.4n)] \leq y \leq [x/(1.6n)].$$

[0012]

## [EXAMPLE 4]

Sr, La and Co were selected as the A element, the R element and the



M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{ZnO}$  were formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{Zn}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0.117$ ,

5 wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of  $0.7\ \mu\text{m}$  in average diameter. Added as sintering aids at an early stage of the fine pulverization of the coarse powder were  
10 0-0.60 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as  $\text{CaO}$ ), based on the weight of the coarse powder. Each of the resultant fine powder slurries was wet-molded in a magnetic field of 10 kOe, and each of the resultant green bodies was sintered at  $1180$ - $1230^\circ\text{C}$  for 2 hours. Each of the resultant sintered bodies was machined to a shape of about 10  
15  $\text{mm} \times 10\ \text{mm} \times 20\ \text{mm}$  to measure magnetic properties by a B-H tracer. The results are shown in Fig. 2. Incidentally, when  $\text{SiO}_2$  was 0 weight %, the value of  $i\text{Hc}$  was extremely too low to plot it.

It is clear from Fig. 2 that as the amount of  $\text{SiO}_2$  added increases, the  $i\text{Hc}$  increases, and when the amount of  $\text{SiO}_2$  added is 0.45 weight %, an  
20 appropriate value of  $i\text{Hc}$  is obtained. On the other hand, when the amount of  $\text{SiO}_2$  added increases to 0.60 weight %, the dependency of  $i\text{Hc}$  on the sintering temperature becomes unstable. This seems because the effect of  $\text{SiO}_2$  to suppress the crystal grain growth is excessively suppressed so that proper grain growth does not take place at the sintering step. Accordingly,  
25 it is understandable that the amount of  $\text{SiO}_2$  added is preferably between

0.40 and 0.50 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %.

The above results were obtained in the case of  $n = 5.85$ . However, since the range of the amount of  $\text{SiO}_2$  added depends on the value of  $n$ ,  
 5 similar investigations have been carried out when the value of  $n$  is 5.95. In this case ( $n = 5.95$ ), it has been found that the amount of  $\text{SiO}_2$  added is preferably between 0.20 and 0.50 weight %.

The dependency of magnetic properties on the amount of  $\text{CaO}$  added has been investigated, when the amount of  $\text{SiO}_2$  added is fixed to be  
 10 0.45 weight %. The results are substantially same as those mentioned above. As a result, it has been found that the amount of  $\text{CaO}$  added is preferably between 0.35 and 0.55 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %.

Next, as the results of investigation in connection with the influence  
 15 of the amount of the combined addition of  $\text{SiO}_2$  and  $\text{CaO}$  on the magnetic properties of the sintered body produced by the method in the same manner as in EXAMPLE 4 except that  $\text{Co}$  was selected in place of  $\text{Zn}$  as the  $M$  element, it has been found that the amount of  $\text{SiO}_2$  added is between 0.20 and 0.50 weight % and the amount of  $\text{CaO}$  added is between 0.35 and 0.50  
 20 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %.

[0013]

[EXAMPLE 5]

$\text{La}$  was selected as the  $R$  element, and  $\text{Mn}$ ,  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Zn}$  were  
 25 selected as the  $M$  element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and

oxides of the M elements were formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3]$  by atomic ratio,  
wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0.117$ ,

5 wet-mixed, and then calcined at 1200°C for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of 0.7  $\mu\text{m}$  in average diameter. Added as sintering aids at an early stage of the fine pulverization of the coarse powder were  
10 0.45 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as  $\text{CaO}$ ), respectively, based on the weight of the coarse powder. Each of the resultant fine powder slurries was wet-molded in a magnetic field of 10 kOe, and each of the resultant green bodies was sintered at 1180-1230°C for 2 hours. Also, as COMPARATIVE MATERIAL (CONVENTIONAL  
15 FERRITE MAGNET), a ferrite composition in which  $n = 6.0$  and  $x = y = 0$  in the above basic composition was produced in the same manner. Each of the resultant sintered bodies was machined to a shape of about 10 mm  $\times$  10 mm  $\times$  20 mm to measure magnetic properties by a B-H tracer. The results are shown in Fig. 3.

20 It is understood from Fig. 3 that residual magnetic flux density  $B_r$  of each material replaced with Mn, Ni or Zn (Mn-, Ni- or Zn-containing ferrite magnet) extends favorably in a low  $iH_c$  region as compared with that of the conventional ferrite magnet, its effect on the improvement in saturation magnetization ( $\sigma_s$ ) is remarkably increased. Accordingly, the  
25 material replaced with Mn, Ni or Zn (Mn-, Ni- or Zn-containing ferrite

magnet) is particularly suitable for the high Br ferrite magnets. On the other hand, the material replaced with Co (Co-containing ferrite magnet) has both a comparatively favorable value of Br and a high value of iHc, so that it is utmost promising for the high performance ferrite magnets. As  
 5 shown in this EXAMPLE, it is clear that the invented materials are advantageous over the conventional ferrite magnets.

Incidentally, also in the sintered body produced in the same manner as in EXAMPLE 5 except that BaCO<sub>3</sub> is used in place of SrCO<sub>3</sub> in the mixing step before calcination, that is, in the invented material selected Ba  
 10 as the A element, the same effects may be expected.

[0014]

[EXAMPLE 6]

La and Co were selected as the R element and the M element, respectively, and SrCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> were formulated to  
 15 provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{Co}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0.3$ ,

wet-mixed, and then calcined at 1200°C for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and  
 20 then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of 0.73 μm in average diameter. Also, a slurry containing fine powder of 0.43 μm in average diameter was produced using a sand mill. On this occasion, added as sintering aids at an early stage of the fine pulverization of the coarse powder were 0.45 weight % of SiO<sub>2</sub> and  
 25 0.80 weight % of CaCO<sub>3</sub> (0.45 weight % as CaO), based on the weight of

the coarse powder. The resultant fine powder slurries containing the fine powder of  $0.73\ \mu\text{m}$  was wet-molded without alternation in a magnetic field of 10 kOe to obtain a green body. On the other hand, the resultant fine powder slurries containing the fine powder of  $0.43\ \mu\text{m}$  was dried, and then  
5 subjected to milling treatment. The milling was carried out by using a kneader so that the concentration of a solid component became 85 weight % by adding water thereinto. On this occasion, to improve the dispersibility, a salt of polycarboxylic acid was added in the amount of 0.4 weight % per a solid component in the fine powder slurry. Thereafter, the  
10 sintered body was produced in the same manner as in the case of the fine powder of  $0.73\ \mu\text{m}$ . Each of the resultant green bodies was sintered at  $1180\text{--}1230^{\circ}\text{C}$  for 2 hours to produce a sintered body. Also, a sample having a composition of  $x = y = 0$  in the above basic composition was produced as a COMPARATIVE MATERIAL (CONVENTIONAL POWDER)  
15 in the same manner. Each of the resultant sintered bodies was machined to a shape of about  $10\ \text{mm} \times 10\ \text{mm} \times 20\ \text{mm}$  to measure magnetic properties by a B-H tracer. The results are shown in Fig. 4.

It is clear from Fig. 4 that both in  $0.73\ \mu\text{m}$  and in  $0.43\ \mu\text{m}$ , the magnetic properties of the material replaced with La and Co (La,  
20 Co-containing powder) are advantageous over the conventional powder. Particularly, the improvement in  $iH_c$  is excellent. Further, the material fine pulverized to a  $0.43\ \mu\text{m}$  level and subjected to milling treatment shows improvement in Br by about 150G, thereby revealing the validity of the method recited in claim 5.

25 As the results of further detailed investigation on the influence of the

average diameter of a finely pulverized powder on the magnetic properties, it has been revealed that the average diameter exceeding  $0.7\ \mu\text{m}$  leads to remarkably decrease in the validity of the above method, so that the average diameter of less than  $0.40\ \mu\text{m}$  results in conversely decrease in the magnetic properties because excessive crystal grain growth takes place at the sintering step. Accordingly, the average diameter of a fine powder after fine pulverization is preferably between  $0.40$  and  $0.70\ \mu\text{m}$ .

Also, as the results of further detailed investigation on the influence of the amount of a dispersant added at the time of milling step on the magnetic properties, it has been revealed that the amount of the dispersant of  $0.2$  weight % per a solid component does not provide remarkably the effectiveness, and the amount of the dispersant exceeding  $2.0$  weight % per a solid component results in conversely deterioration in magnetic properties due to the decomposition of organic substances at the time of sintering step. Accordingly, the amount of a dispersant added is preferably between  $0.20$  and  $2.0$  weight %.

[0015]

[EXAMPLE 7]

$\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  were formulated to provide a basic composition of  $\text{SrO} \cdot n\text{Fe}_2\text{O}_3$ , wherein  $n = 5.95$ , wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of  $0.80\ \mu\text{m}$  in average diameter. At an early stage of the fine pulverization of each coarse powder,  $0$ - $5.0$  weight % of  $\text{La}_2\text{O}_3$  and  $0$ - $2.3$

weight % of CoO, based on the weight of the coarse powder, were added.

Also, 1.3 weight % of Cr<sub>2</sub>O<sub>3</sub> was added at an early stage of the fine pulverization of coarse powder to produce a slurry as a comparative

material. In any cases, 0.50 weight % of SrCO<sub>3</sub>, 0.30 weight % of SiO<sub>2</sub>

5 and 0.80 weight % of CaCO<sub>3</sub> (0.45 weight % as CaO), based on the weight of the coarse powder, were added as sintering aids. When 2.50 weight % of La<sub>2</sub>O<sub>3</sub> and 1.15 weight % of CoO were added, the final composition to be obtained corresponds to a basic composition approximately represented by the following formula:

10  $(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{Co}_y)_2\text{O}_3]$  by atomic ratio,  
wherein  $x = 0.15$ ,  $y = x/2n$ , and  $n = 5.83$ .

Each of the resultant fine powder slurries containing fine powders of an average diameter of 0.80 μm was wet-molded without alternation in a magnetic field of 10 kOe to obtain a green body. Each of the resultant  
15 green bodies was sintered at 1180-1230°C for 2 hours to obtain a sintered body. The resultant sintered body was machined to a shape of about 10 mm × 10 mm × 20 mm to measure magnetic properties by a B-H tracer. The results are shown in Fig. 5.

It is clear from Fig. 5 that the addition of 2.50 weight % of La<sub>2</sub>O<sub>3</sub>  
20 and 1.15 weight % of CoO (indicated by “∇”) greatly improves iHc as compared with no addition (indicated by “○”), with extremely smaller decrease in Br in a high iHc region than in the case of the addition of Cr<sub>2</sub>O<sub>3</sub> that is usually added to increase iHc (indicated by “×”). Further, the useful magnetic property (iHc) could not be obtained when only CoO was

added (indicated by “ $\triangle$ ,  $\square$ ”), or when the balance of charge compensation was destroyed (indicated by “ $\diamond$ ”).

This EXAMPLE has not only clarified the effectiveness of the present invention in the case of  $R = \text{La}$  and  $M = \text{Co}$ , but also proved that the effectiveness obtained by adding the R element and the M element at the time of fine pulverization to provide approximately the desired basic composition is substantially same as that obtained by adding the R element and the M element at the time of calcination to provide the desired basic composition.

[0016]

Although the above EXAMPLES are related to Sr ferrite replaced with the R element and the M element, it should be noted that the same effectiveness may be expected also in Ba ferrite replaced with the R element and the M element.

[0017]

### **Effects of the Invention**

As mentioned above, the present invention provides a ferrite magnet having substantially a magnetoplumbite-type crystal structure and also showing higher saturation magnetization and/or coercivity than those of conventional ferrite magnets, thereby greatly contributing to the development in the wide ranges of magnet applications as a new ferrite magnet excellent in cost performance.

### **Brief Description of the Drawings**



[Fig. 1] Fig. 1 is a graph showing an example of the correlations between  $x$  and  $\sigma_s$ ,  $H_c$  in the ferrite magnet of the present invention.

[Fig. 2] Fig. 2 is a graph showing an example of the correlations between the amount of  $\text{SiO}_2$  added, the amount of  $\text{CaO}$  added, and magnet  
5 properties in the ferrite magnet of the present invention.

[Fig. 3] Fig. 3 is a graph showing an example of magnetic properties of the ferrite magnet of the present invention.

[Fig. 4] Fig. 4 is a graph showing the effectiveness of a method according to the present invention.

10 [Fig. 5] Fig. 5 is a graph showing an example of favorable magnetic properties of the ferrite magnet of the present invention.

## ABSTRACT

### Problems to be solved:

To provide a ferrite magnet having higher magnetic properties than  
 5 those of conventional ferrite magnets and a method for producing thereof.

### Solution:

To determine each amount of raw material oxides to be added to  
 meet the conditions for providing the ferrite magnet having a basic  
 composition represented by the following general formula:

10  $(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one element selected  
 from the group consisting of La, Nd and Pr, La being an indispensable  
 element, M is at least one element selected from the group consisting of  
 Mn, Co, Ni and Zn, Co being an indispensable element, and x, y and n are  
 15 numbers meeting the following conditions:

$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5.4 \leq n \leq 6.0.$$

Particularly, to produce the above ferrite magnet having excellent  
 20 magnetic properties by subjecting a raw material powder having the above  
 basic composition to pulverizing until the average diameter of the powder  
 mixture becomes 0.4-0.7  $\mu\text{m}$ , thereafter drying or concentrating, milling,  
 and then to molding in a magnetic field and sintering.

**Selected Drawings:** Fig. 5

FIG. 1

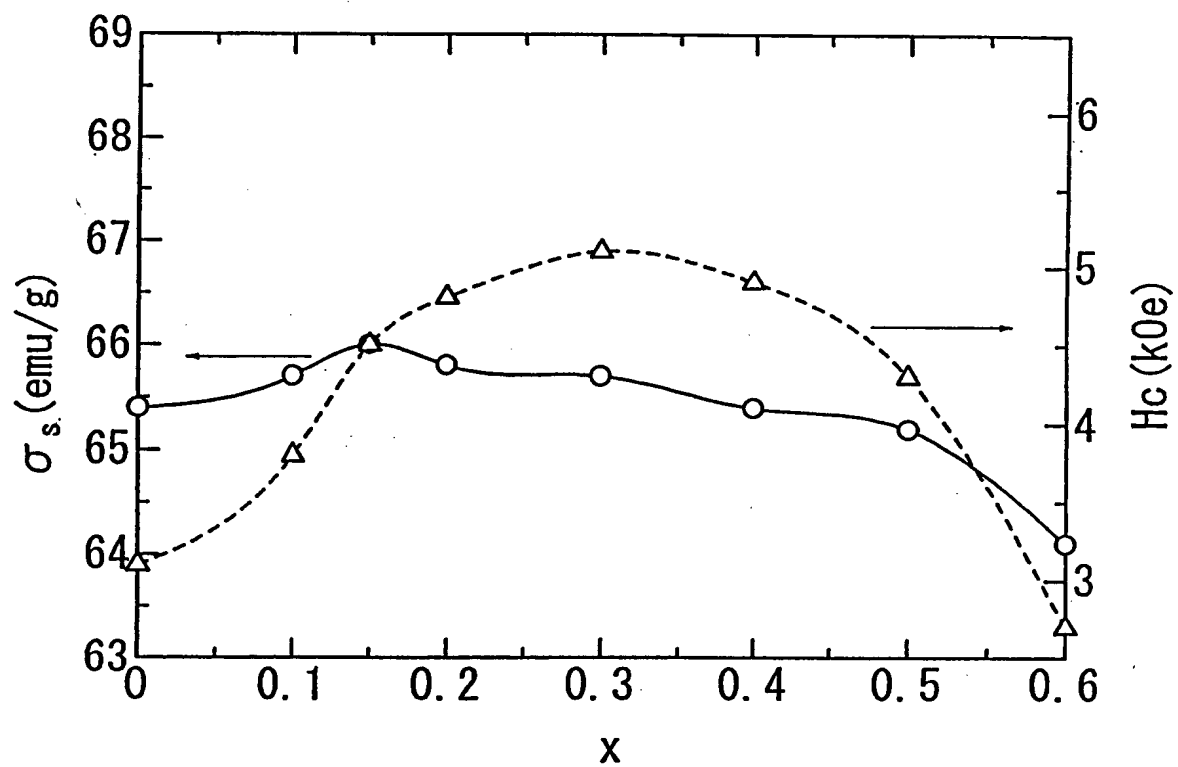


FIG. 2

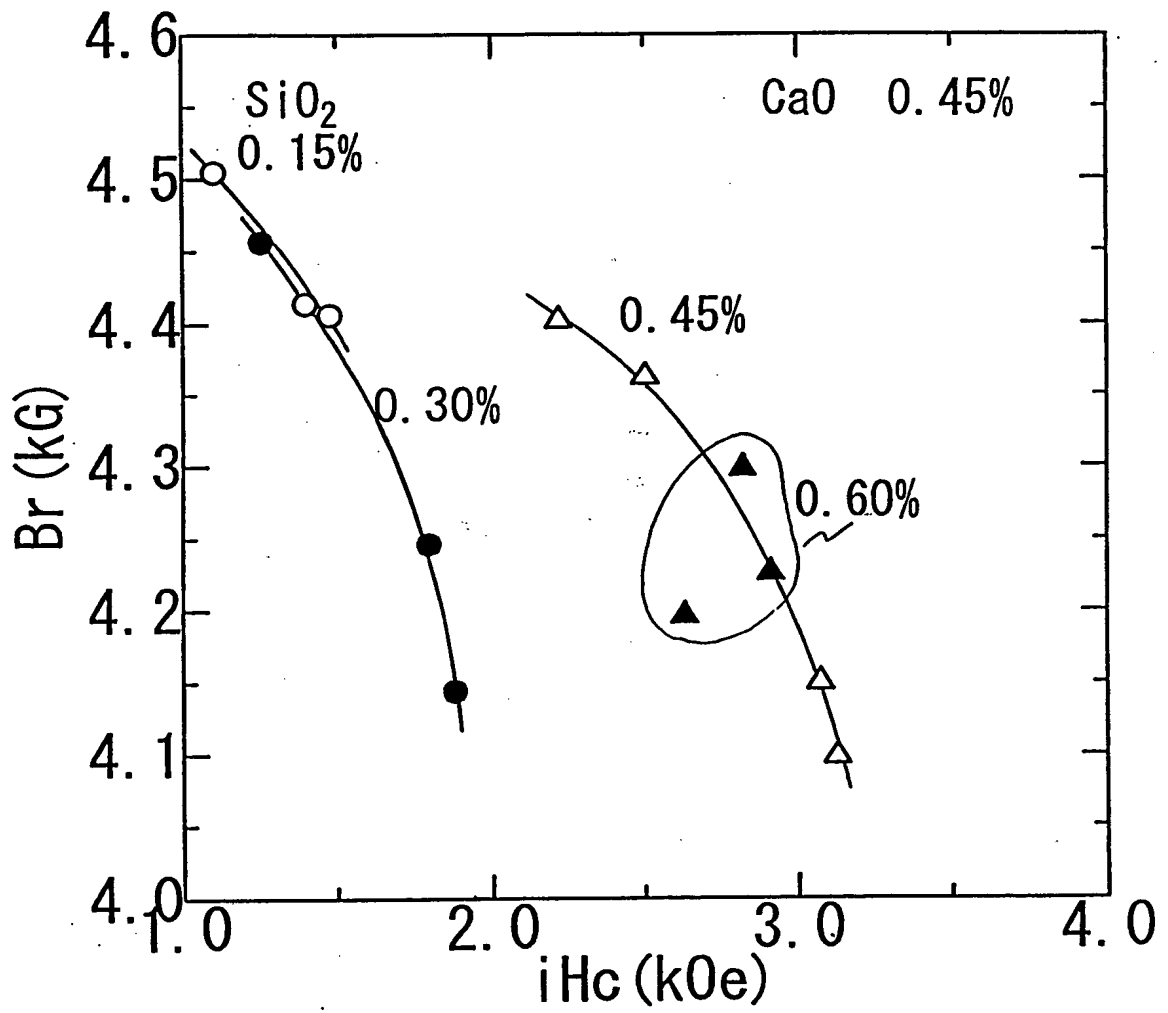


FIG. 3

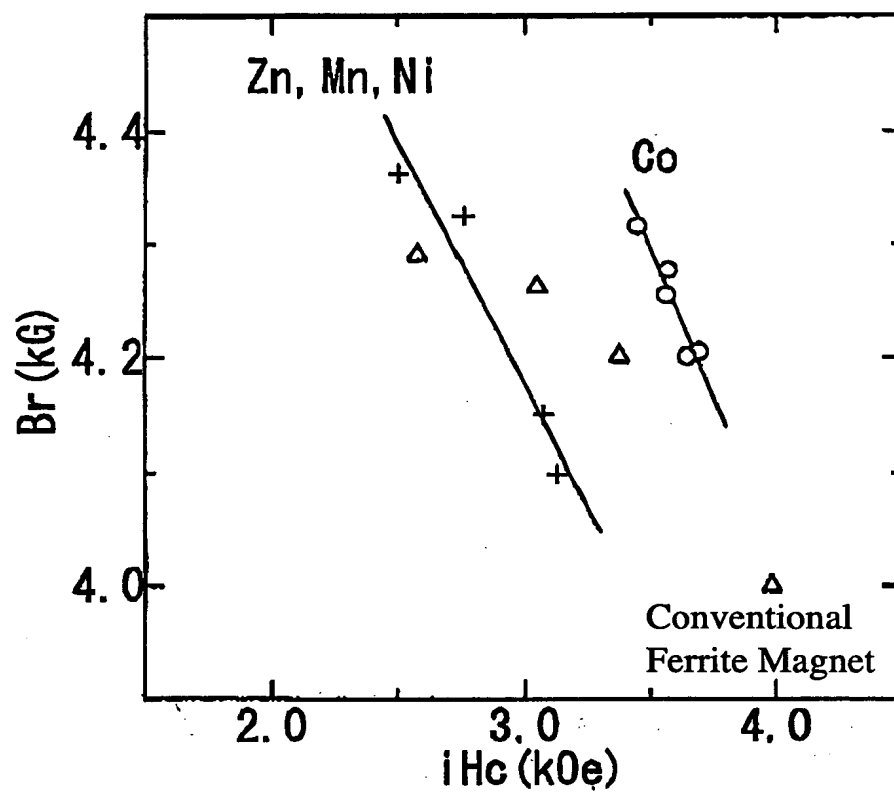


FIG. 4

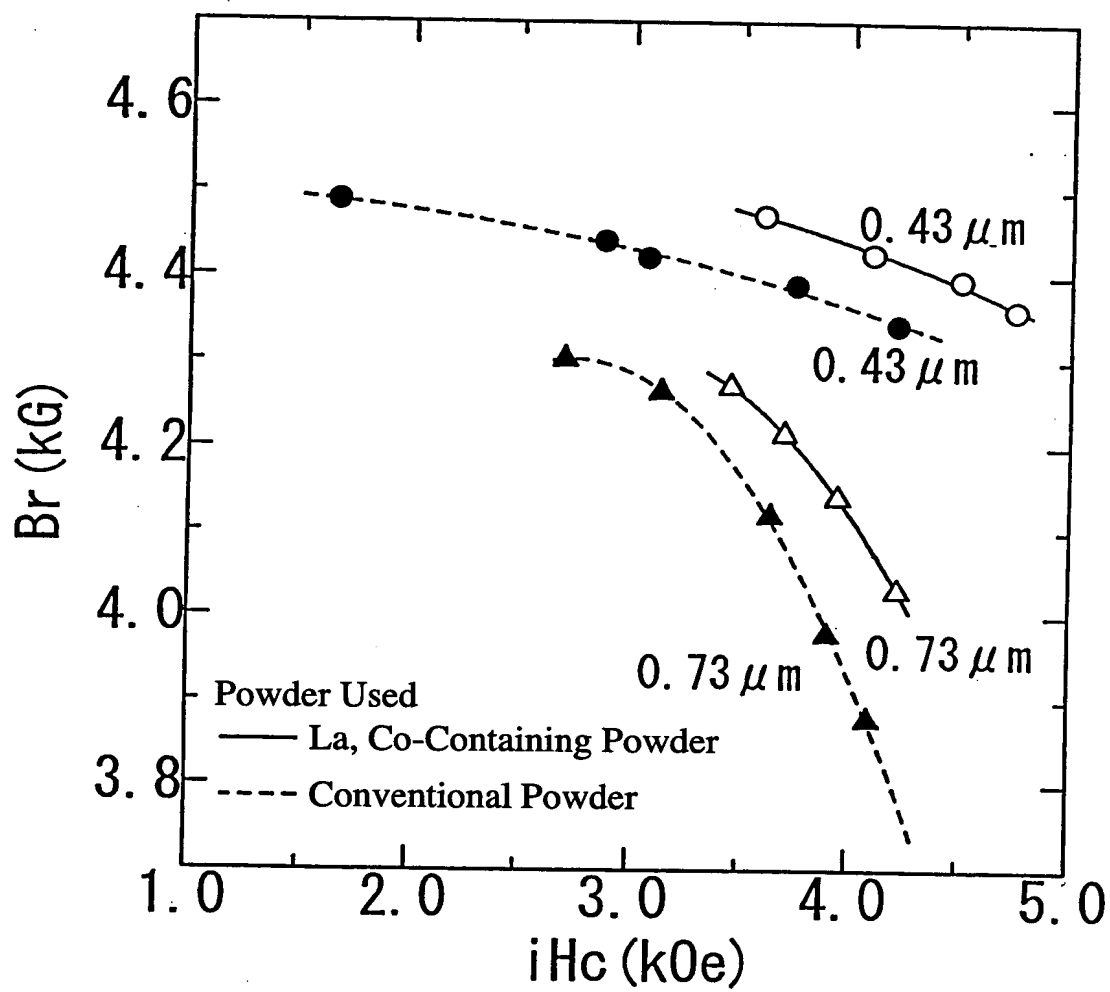


FIG. 5

